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PHYSICO-CHEMICAL STUDIES AT PRESSURES

BY

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Introduction

Studies of physical chemistry at high pressure were started at the Physico-chemical Laboratory, Department of Chemistry, Faculty of Science, Kyoto University, in 1940 and since 1948 these studies have been the main interest of the laboratory. The result of these investigations had been reviewed in journals.¹⁾²⁾³⁾ The effect of high pressure has been studied in various fields of physical chemistry. Recent studies are summarized under each article in the present paper.

Diffusion

Compressibilities, Solubilities and etc. in liquids phases had been studied.¹⁾ We have measured diffusion rate by the capillary cell method; the self-diffusion of benzene,⁴⁾ methanol⁵⁾ and ethanol⁶⁾ were studied using C¹⁴ as the tracer and also the diffusion of iodine or sulphur in benzene.⁴⁾ The capillary cell, one end of which was sealed, was 4 cm in length and 0.02~0.1 ml in volume. It was placed perpendicularly at the bottom of the high pressure vessel. Pressure was applied to the samples with mercury as the pressure transmitting fluid by means of a hand pump.

The diffusion coefficient D is given by the following equation :

$$\frac{Dt}{l^2} = \frac{4}{\pi^2} \ln \left[\frac{8}{\pi^2} \frac{C_0}{C_{av}} \sin^2 \frac{\pi}{2} (1 - \beta p) \right],$$

where C_{av} is the average concentration of diffusing material in the cell at time t and β the compressibility.

One of the results obtained with methanol is shown in the following table.

Diffusion coefficients of methanol				
pressure (kg/cm ²)	Temp. °C	15	25	40
1		1.84	2.21	3.01
500		—	1.90	2.55
1,000		1.24	—	2.07
3,000		1.77		

The diffusion coefficients of the other materials mentioned above have been evaluated in a similar way.

From these results, the activation energy ΔE_v , which can be obtained as the temperature coefficient of diffusion, and the activation volume ΔV^\ddagger , which is the pressure coefficient, are calculated as follows:

	in C_6H_6			in CH_3OH
	S_8	I_2	C_6H_6	CH_3OH
ΔE_v (kcal)	0.86	1.23	0.78	2.7
ΔV^\ddagger (cc/mole)	29	15	22	—

On methanol the diffusion coefficient increases abnormally at 3000 kg/cm². It would be very interesting to know whether this results from the formation of hydrogen bonds as in the case of water.

The self-diffusion of ethanol up to several hundred atmosphere has also been measured and some results of a similar tendency to those of methanol have been obtained.

In the gaseous phase, we have measured the diffusion coefficient in the system CO_2-O_2 .⁷⁾

In parallel with these studies, the thermal diffusion was studied in H_2-CO_2 mixture using a perpendicular cell which consisted of two parts, the upper one being kept at a higher temperature and the lower one at a lower temperature.

After about 100 hours at temperature difference of about 100°C, equilibrium was reached and the change of the composition was measured by chemical analysis and ultrasonic interferometer in the pressure range of 1 to 120 atm. From the results thus obtained, the thermal diffusion factor α increases to about 10 atm, but shows a inverse tendency above 40 atm and decreases abruptly at 100 atm. It is considered that this decreases is probably related to the pseudo-critical temperature.⁸⁾⁹⁾

Infra-red Absorption

As one of the studies on the behavior of gases at high pressure, the relations of P - V - T and the viscosities of various gases had been measured.

Pressure effects on infra-red absorption appear at pressures of more than several ten atmospheres and are interesting projects, because they enable us to investigate the nature of gases at high pressure.

The beginning of these studies was marked by the discovery of the induced absorption spectrum of gaseous acetylene. In this gas the vibration (ν_2) is symmetrical and is therefore inactive in infra-red absorption, but it appears as an induced

absorption band at high pressure. It has been shown that the absorption intensity is proportional to the square of the density and also that the pressure effects of the perturbing gases such as N_2 , Ar, H_2 and O_2 are proportional to their molecular polarizabilities.

From these observations it can be concluded that the pressure induced absorption is caused by the interaction between the colliding molecules at binary collision. In this laboratory such induced absorptions of C_2H_2 , CO_2 , and C_2H_4 have been investigated.¹⁰⁾¹¹⁾

Subsequently the relation between the infra-red absorption and pressure has been studied on polar molecules such as CH_3Br . In this case it has been shown that the regularity of fine structure of absorption band increases with pressure.¹²⁾

Solid State

Information about the strength of materials is essential for the design of high pressure apparatus, but it is also interesting from a theoretical point of view.

We have studied the influence of pressure on the mechanical properties of single crystals of alkali halides, which are important for their application in optical windows of high pressure vessel, and which are also of great theoretical interest because of their simple structure.

The amount of plastic deformation by pressure increase in the order, $LiF < NaCl < KCl < KBr < KI$ and from the analysis of the results obtained, it was shown that the mean free path of the dislocation was $2.1 \cdot 10^{-4} \sim 1.5 \cdot 10^{-3}$ cm. The process of plastic deformation by pressure was also examined.¹³⁾¹⁴⁾¹⁵⁾

On the single crystal of $AgCl$, the relations between the lattice defects and pressure were studied by measuring the ionic conductivity. The rate of decrease (recovery) of the conductivity was measured by the capacitance bridge method on the sample, which was highly conductive after the plastic deformation. Its temperature coefficient was determined from the temperature dependence and the mechanism of this process was discussed. The effects of the hydrostatic pressure on the ionic conductivity were further investigated up to 700 kg/cm^2 .

From the results obtained the pressure coefficient of the conductivity was determined and the observed values were compared with the values calculated from the following equation.

$$\left(\frac{\partial \ln \sigma}{\partial P} \right)_T = - \frac{\ln(BC)\chi}{\alpha T},$$

where σ is the ionic conductivity, χ the compressibility of the crystal, and α the coefficient of thermal expansion. B and C are numerical factors,

The value of the coefficient σ are $-3.0 \times 10^{-4} \text{ cm}^2/\text{kg}$ in the intrinsic range of temperature, from 90°C to 110°C and $-2.2 \sim -2.5 \times 10^{-4} \text{ cm}^2/\text{kg}$ in the extrinsic range, from 30°C to 50°C , depending on the temperature of measurement.

These values are in good agreement with the calculated values and it is shown that these depend on the formation of the charge carriers and their mobility.¹⁶⁾¹⁷⁾ Additional studies on the effects of pressure on the conductivity of NaCl are in progress.¹⁸⁾

Rate Processes

The influence of high pressure on biochemical systems can also be the object of physicochemical studies. In this field, the denaturation of protein is one of the most interesting problem.

We have measured the denaturation of protein such as egg albumin and hemoglobin kinetically. The rate of the denaturation of egg albumin was examined under pressures of $1 \sim 9,000 \text{ kg/cm}^2$ and at temperatures of $10 \sim 75^\circ\text{C}$ to determine the temperature coefficient at constant pressure (activation energy) and the pressure coefficient at constant temperature. It was found that the coefficients changed their signs over the range of measurements.¹⁹⁾²⁰⁾

ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger are calculated according to absolute reaction rates and the mechanism of denaturation is discussed.²¹⁾

This research is being further continued with various proteins and different experimental methods.²²⁾²³⁾

The explosion and oxidation reactions of simple unsaturated organic compounds have been studied on C_2H_2 and C_2F_4 . The effects of various added substances on the explosion limits were determined by varying pressure and temperature over a wide range²⁴⁾ The same kind of study was done on C_2H_4 too,²⁵⁾ and the character of explosion of high pressure gases was discussed.²⁶⁾

The explosion and oxidation reactions of propylene and acrolein was studied at high and low pressures.²⁷⁾ Generally, a third explosion limit is observed in these systems which is called 'the thermal explosion limit'.

The explosion peninsula, the region bounded by the first and second pressure limits of explosions, is found in the range of lower pressure and high temperature for these gases (C_2H_4 , C_3H_6 and $\text{C}_3\text{H}_4\text{O}$). It is concluded that in the region of the explosion peninsula, mainly carbon monoxide is formed during the induction period.²⁸⁾ The mechanism of the formation of CO is an interesting problem and is now being studied in detail.

Explosion limits of high pressure gases

	C ₂ H ₂		C ₂ H ₄		C ₂ F ₄		C ₃ H ₆	
	O ₂	Air	O ₂	Air	O ₂	Air	O ₂	Air
Pressure (kg/cm ²)	10	30	80	20	100	50	15	15
Lowest explosion temp. (°C)	220	210	240	280	120	140	265	265

Reaction at High Pressure and High Temperature

An apparatus for the reaction at high pressure and high temperature was constructed, using piston-cylinder type vessel made of tungsten carbide and which contained carbon tube heater covered with talc.

Studies on the reactions at high pressure and high temperature can be performed by this apparatus up to the temperature of 2000°C and to the pressure of 20,000 atm.

In this apparatus we achieved a direct synthesis between boron and phosphorus, a reaction which does not occur under ordinary conditions.

Reaction between boron and phosphorus took place at temperatures of 1000° ~ 1500°C and at a pressure of 10,000 atm.²⁹⁾

The compound formed is a gray powder. By X-ray diffraction the crystal is shown to have a face centered cubic lattice with a mean lattice distance of 4,530 Å.

According to the diffraction intensities, it belongs to the ZnS type with a composition of BP, as confirmed by chemical analysis.

Some electric measurements on the new compound are compiled in the following table :

2θ	d (Å)	$h^2+k^2+l^2$	(hkl)	a (Å)
34.26	2.619	3	111	4.536
39.92	2.258	4	200	4.516
57.62	1.599	8	220	4.523
68.85	1.364	11	113	4.524
72.35	1.306	12	222	4.526
85.82	1.132	16	400	4.528
95.55	1.041	19	133	4.538
98.98	1.014	20	240	4.535
112.75	0.926	24	224	4.536
124.01	0.873	27	333	4.537

electric resistance

at -107°C

$9.0 \times 10^{-3} \Omega \text{ cm}$

at room temperature

$4.4 \times 10^{-3} \Omega \text{ cm}$

Hall coefficient	$R_H = 2.03 \text{ cm}^3/\text{coulomb (} p\text{-type)}$
Carrier concentration	$n \doteq 3.6 \times 10^{18} \text{ cm}^{-3}$
Hall mobility	$\mu \doteq 230 \text{ cm}^2/\text{volt cm}$

The new III-V compound is shown to be a semiconductor of *p*-type.

Impurities contained in the compound are found to be mainly Mg by the spectroscopic analysis.

Further studies on this subject are in progress.

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